

Electrochemical preparation and properties of nanostructured Co_3O_4 as supercapacitor material

Mustafa Aghazadeh

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Abstract Nanostructured Co_3O_4 was prepared via a simple two-step process: cathodic electrodeposition of cobalt hydroxide from additive free nitrate bath and then heat treatment at 400 °C for 3 h. The prepared oxide product was characterized by powder X-ray diffraction, infrared spectroscopy, surface area measurement, scanning electron microscopy, and transmission electron microscopy. Morphological characterization showed that the oxide product was composed of porous nanoplates, and BET measurement displayed that the oxide plates have the average pore diameter and the surface area of 4.75 nm and 208.5 m² g⁻¹, respectively. The supercapacitive performance of the nanoplates was evaluated using cyclic voltammetry and charge–discharge tests. A specific capacitance as high as 393.6 F g⁻¹ at the constant current density of 1 A g⁻¹ and an excellent capacity retention (96.5% after 500 charge–discharge cycles) was obtained. These results indicate that Co_3O_4 nanoplates can be recognized as high-performance electrode materials.

Keywords Crystalline Co_3O_4 · Cathodic electrodeposition · Heat treatment · Microstructure · Supercapacitors

1 Introduction

Among the transition oxides, cobalt oxide (Co_3O_4) has been widely used in many fields, such as pigment for glasses and ceramics, solid-state sensors, heterogeneous

catalysts, and electrochromic devices [1–3]. It is also regarded as a newly invented implement in supercapacitors [4–7]. An emerging application of Co_3O_4 , as an electrode material in electrochemical supercapacitors, can prove itself as a promising alternative to expensive RuO_2 .

Compared with the other methods in use for the synthesis of metal oxide and hydroxide nanostructures, the electrodeposition of these materials is simple and highly subtle. This method has received more attention due to its inexpensive equipment, simple procedure, and mild deposition conditions. An easy control of oxide morphology and composition is possible via bath conditions and electrochemical parameters, such as applied potential and current density [8–14].

Nowadays, considerable interest has been developed in producing high energy and power density electrochemical capacitors. Nanostructured Co_3O_4 can offer large surface area, high conductivity, electrochemical stability, and pseudocapacitive behavior. Thus, it can contribute significantly to this technology. Therefore, much research is devoted to the synthesis of Co_3O_4 nanostructures and to the control of their microstructure. Recent reports have proved that Co_3O_4 with special microstructure and morphology displayed excellent electrochemical capacitive behavior [15–23]. For example, a specific capacitance of 227 F g⁻¹ for hexagonal Co_3O_4 nanosheets was reached through a complex-precursor solution procedure and sequential thermal decomposition at atmospheric pressure [15]. Crater-like Co_3O_4 microspheres with a BET surface area of 60 m² g⁻¹ were prepared by casting from mesoporous silica material MCM-41. They exhibited a specific capacitance of 102 F g⁻¹ at a sweep rate of 3 mV s⁻¹ [16]. Single crystal Co_3O_4 nanorods, which were used as electroactive materials for the supercapacitor, exhibited a high capacitance of 456 F g⁻¹ [17]. The specific capacitance of

M. Aghazadeh (✉)
Materials Research School, NSTRI, P.O. Box 14395-836,
Tehran, Iran
e-mail: mustafa.aghazadeh@gmail.com

Co_3O_4 thin films deposited on glass substrate by spray pyrolysis is 74 F g^{-1} [18], whereas its value for thin films prepared via electrochemical precipitation could reach 164 F g^{-1} [19]. Lin et al. [23] prepared cobalt oxide xerogels by a sol–gel technique followed by a heating step to different temperatures. A maximum capacitance of 291 F g^{-1} was obtained for the CoO_x xerogel calcined at 150°C .

Herein, we report on the preparation of high surface area Co_3O_4 nanoplates via a two-step method; cathodic electrodeposition of cobalt hydroxide from additive-free nitrate bath followed by heat treatment at 400°C for 3 h. The prepared oxide is used as electroactive material for supercapacitors. Its capacitive behavior was investigated in 1 mol L^{-1} KOH electrolyte by cyclic voltammetry (CV) and galvanostatic charge–discharge tests.

2 Experimental procedure

Cobalt oxide was prepared by cathodic electrodeposition from an additive-free aqueous $0.005 \text{ M Co(NO}_3)_2$ bath at 60°C followed by heat treatment at dry air atmosphere. The electrochemical cell included a cathodic stainless-steel substrate centered between two parallel graphite anodes. The deposition experiments were carried out in galvanostatic mode at a current density of 1 mA cm^{-2} for 30 min. The obtained hydroxide film was scrapped from the steel electrode and then heat treated at 400°C for 3 h. The crystal structure of the prepared oxide was determined by powder X-ray diffraction (XRD, Phillips PW-1800) using $\text{Cu K}\alpha$ radiation. The morphology of the prepared samples was observed by scanning electron microscope (SEM, LEO 1455 VP) and transmission electron microscope (TEM, Phillips EM 2085) with an accelerating voltage of 100 kV . The IR spectrum was obtained using a Bruker Vector 22 FT-IR spectrometer. The measurement of specific surface area for the prepared oxide sample was performed through measuring N_2 adsorption–desorption isotherms at 77 K with a Quanta-chrome NOVA-2200e system.

The electrochemical measurements were carried out in a three-electrode electrochemical cell containing 1 M KOH aqueous solution as the electrolyte. Ag/AgCl and platinum electrodes were used as the reference and the counter electrodes, respectively. The working electrode was prepared by pressing the mixture of the prepared oxide sample, acetylene black, conducting graphite, and polytetrafluoroethylene (PTFE) binder (with the weight ratio of 75:10:10:5, respectively) onto a nickel foam current collector. CV and galvanostatic charge–discharge tests were performed by the use of a potentiostat (AUTOLAB®, Eco Chemie, PGSTAT 30). The CV was conducted in a potential range of -0.2 to 0.6 V versus Ag/AgCl at various scan rates. The constant current

charge–discharge test was carried out at a current density of 1 A g^{-1} within a potential range of -0.2 to 0.5 V versus Ag/AgCl .

3 Results and discussion

The XRD pattern of the prepared oxide sample is shown in Fig. 1a. All diffraction peaks in this pattern can be indexed undisputedly to face-centered cubic (fcc) Co_3O_4 phase (JCPDS no. 43-1003). No other phase peaks were observed, demonstrating that the deposited hydroxide was completely transformed into Co_3O_4 after heat treatment at 400°C for 3 h. Besides, the average particle size of about 5 nm was calculated by Scherrer equation using the diffraction peak of (311) plan. The FTIR spectrum of the prepared Co_3O_4 is shown in Fig. 1b. The bands around 568 and 664 cm^{-1} are associated with the OB_3 (B represents Co^{3+} in an octahedral

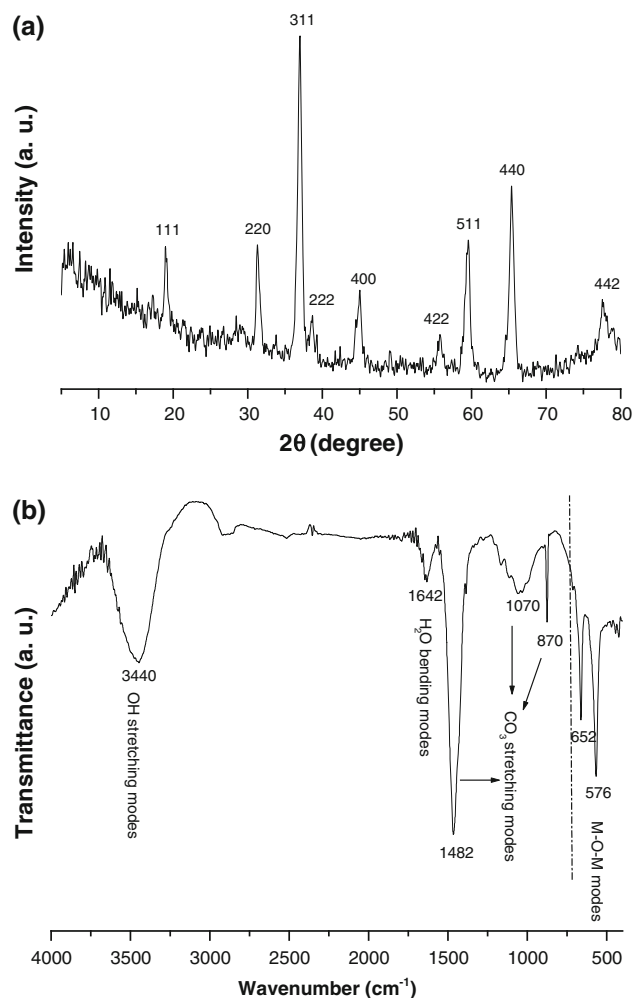


Fig. 1 XRD pattern (a) and IR spectrum (b) of the prepared Co_3O_4 nanoplates

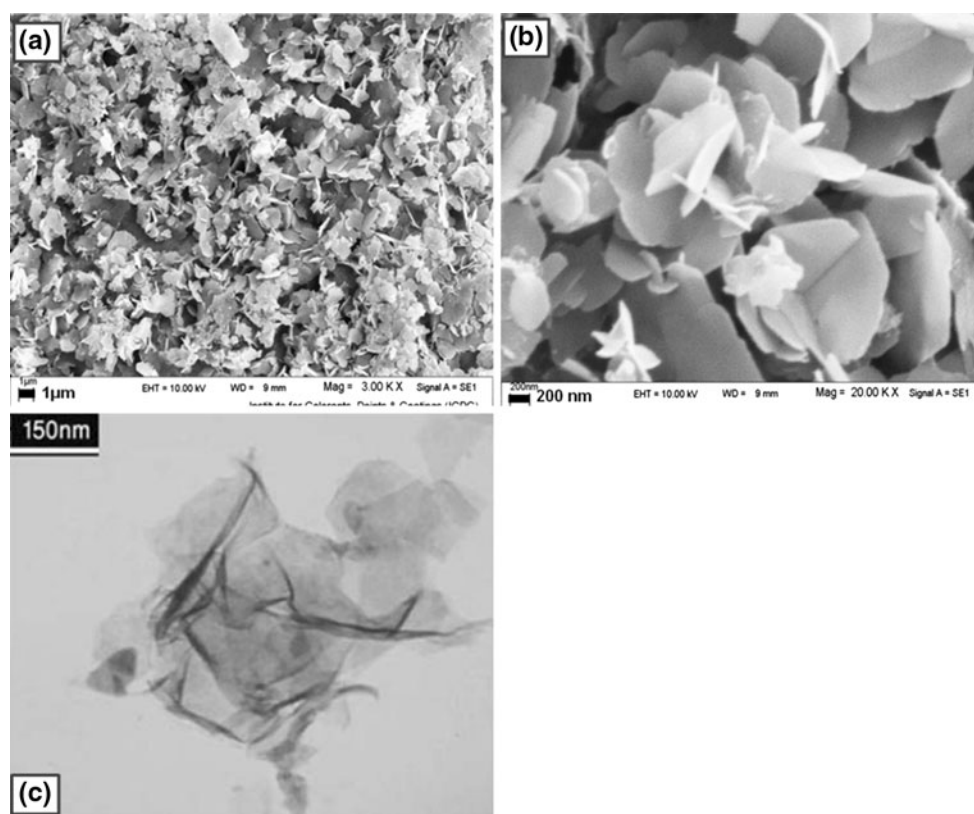


Fig. 2 SEM (a, b) and TEM (c) images of the electrodeposited hydroxide sample

hole) and the ABO (A represents the Co^{2+} in a tetrahedral hole) vibrations in the spinel lattice, respectively [21]. The two bands at $3,440$ and $1,642\text{ cm}^{-1}$ are associated with the hydroxyl groups of molecular H_2O . The peaks at about 1482 , 1070 , and 870 cm^{-1} can be attributed to the carbonate groups originating from the reaction of oxide with CO_2 from air during the analysis procedure.

Morphological characteristics of the prepared cobalt hydroxide and oxide samples are shown in Figs. 2 and 3, respectively. The SEM images of the prepared hydroxide shown in Fig. 2a, b reveal that the prepared hydroxide is composed of discrete plate-like structures in large quantity. High-magnification SEM image (Fig. 2b) clearly indicates that these plate-like structures do not have a perfect hexagonal shape, i.e., they have an irregular shape. This irregularity is also completely evident in edge lengths. In fact, these plate-like structures are more similar to leaf. The edge lengths of the leaf-like structures range from 250 to 450 nm (Fig. 2c). The SEM images in Fig. 3a, b display that the prepared Co_3O_4 has an approximately plate-like morphology. The TEM images in Fig. 3c, d show that these plates are completely porous and have irregularity in their shapes. This morphology can be related to the removal of

structural water from the hydroxide precursor during the heat treatment process.

The surface area of the oxide product was measured using the Brunauer–Emmett–Teller (BET) method. The N_2 adsorption–desorption isotherm at 77 K is shown in Fig. 4, with the inset showing the pore size distribution by the Barrett–Joyner–Halenda (BJH) method. This isotherm has a typical type III form with a type H_3 hysteric loop, indicating the presence of microporous materials according to the IUPAC classification [24]. The H_3 type loops are generally given by the adsorbents with narrow size distribution of uniform pores [25]. Thus, it seems that the prepared Co_3O_4 nanoplates have uniform pores with relative narrow size distribution (inset in Fig. 4). The average pore diameter and the surface area of Co_3O_4 plates were determined as 2.75 nm and $208.5\text{ m}^2\text{ g}^{-1}$, respectively.

Typical CVs for Co_3O_4 electrode at different scan rates in 1 M KOH solution are presented in Fig. 5a. All curves show obvious pseudocapacitance features with similar line-type. A quasi-reversible electron transfer process observed in the CV curves, indicating that the measured capacitance is mainly based on redox mechanism. Within the potential

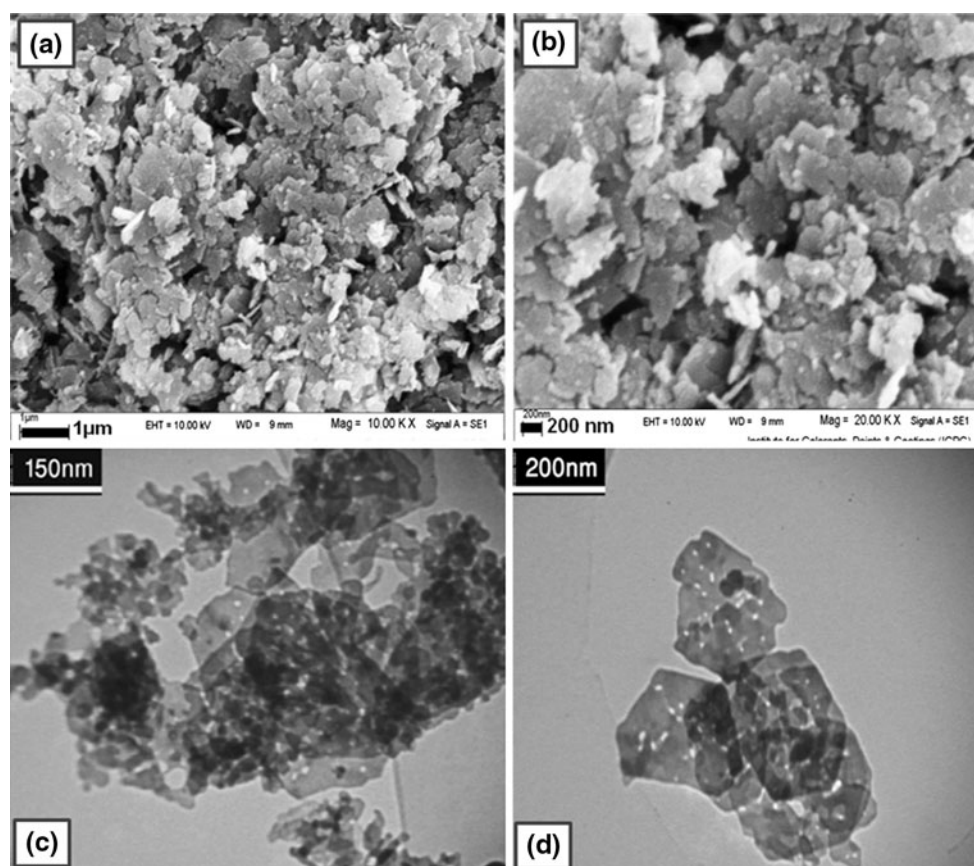
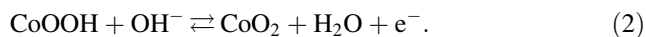


Fig. 3 SEM (a, b) and TEM (c, d) images of the prepared Co_3O_4

scanning range, the electrochemical reactions can be expressed as follows [21, 22]:



The specific capacitance (C) of the oxide can be quantitatively evaluated using the following equation:

$$C = \frac{1}{mv(V_a - V_c)} \int_{V_a}^{V_c} I(V) dV, \quad (3)$$

where C is the specific capacitance of Co_3O_4 (F g^{-1}) measured in the potential range of V_a to V_c , m is the mass of active material (g), v is the scan rate (V s^{-1}) and $I(V)$ is a current response depending on the sweep voltage. The specific capacitance of Co_3O_4 was calculated as 465.5, 410.4, 349.5, and 294.1 F g^{-1} at the scan rates of 5, 10, 25, and 50 mV s^{-1} , respectively.

These values can suggest a relatively high electrochemical utilization and high surface area of the synthesized nanostructures of Co_3O_4 . The electrochemical utilization of the Co_3O_4 electrode can be calculated from $z = C \times \Delta V \times M/F$, where C is the real specific

capacitance (F g^{-1}), ΔV is the potential window (0.8 V in this study), M is the average molecular weight of Co_3O_4 (240.8 g mol^{-1}), and F is the Faradic constant ($96,486 \text{ C mol}^{-1}$). If all of the electro-active sites are involved in the Faradic reactions, the z value corresponds to 1. The above equation gives the z values of 0.92, 0.83, 0.71, and 0.57 for the scan rates of 5, 10, 25, and 50 mV s^{-1} , respectively. These findings show a relatively high ratio contribution of the electro-active sites in the redox reactions, thus giving a high specific capacitance. It is worth noting that the porous morphology of the Co_3O_4 plates (as seen in TEM image, Fig. 3c) caused better electrolyte penetration in the plates and so exhibited high contribution to the redox reactions (Eqs. 1, 2). In comparison with the reported values for the various morphologies of Co_3O_4 [16, 21, 22], the calculated capacitance for the prepared Co_3O_4 nanoplates is relatively high and acceptable.

The prepared Co_3O_4 electrode was galvanostatically discharged at the current density of 1 A g^{-1} for 500 cycles. Figure 5b shows a typical chronopotentiogram including the first ten charge–discharge cycles. The specific capacitance of Co_3O_4 can also be calculated from the following equation:

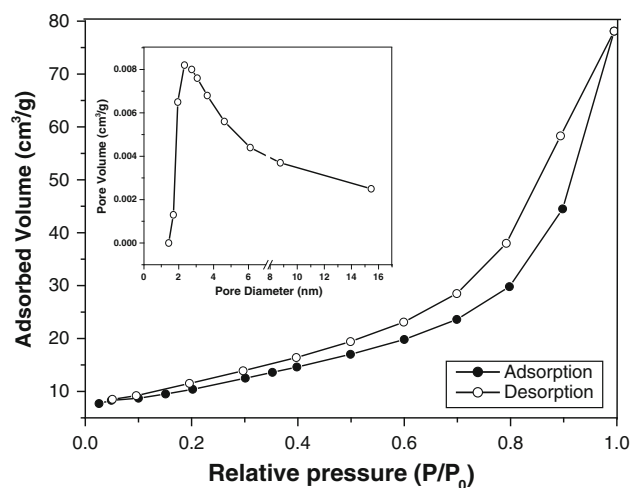


Fig. 4 N₂ adsorption–desorption isotherms of the prepared Co₃O₄ nanoplates. The inset shows their BJH pore-size distribution curve

$$C_m = \frac{C}{m} = \frac{I \times \Delta t}{\Delta V \times m} \quad (4)$$

where I is the applied current (1 A), ΔV is the potential range (2×0.7 V), Δt is the time of a charge–discharge cycle (551 s), and m is the mass of Co₃O₄ (1 g). The calculated capacitance for the 10th cycle was as high as 393.6 F g^{-1} , which is very close to that calculated from the CV curves (Fig. 5a), again confirming the high capacitance of the prepared nanoplates of Co₃O₄. For the 500th cycle, the calculated capacitance was 381.2 F g^{-1} , showing only 3.5% of capacity decay compared with the 10th cycle (Fig. 5c).

The coulombic efficiency (η) was calculated from the galvanostatic charge–discharge tests as follow [26]:

$$\eta = \frac{Q_d}{Q_c} \times 100 = \frac{\Delta t_d}{\Delta t_c} \times 100, \quad (5)$$

where Q_d and Q_c are the electric charge for discharging and charging, respectively. Δt_c and Δt_d are the times of charging and discharging, respectively. According to the Eq. 5, the average coulombic efficiency was calculated to be about 97.5%.

The energy density (E) and power density (P) were calculated by the following equations from the constant current charge/discharge cycles [27, 28]:

$$E = 1/2C(\Delta V)^2, \quad (6)$$

$$P = \frac{E}{t}. \quad (7)$$

Here, C is the capacitance of the capacitor and it is calculated according to Eq. 7; where t and ΔV represent the discharge time and the potential range from the end of the charge to the end of the discharge, respectively. It can be

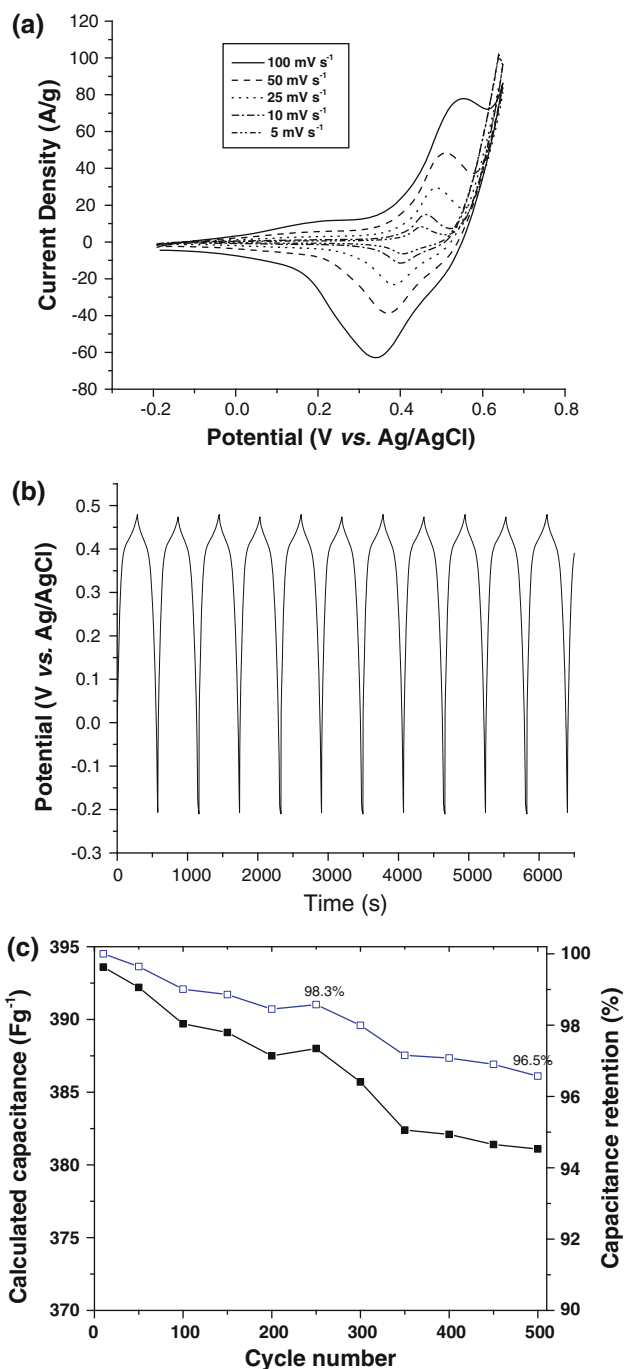


Fig. 5 CV of Co₃O₄ electrode at various scan rates (a), its charge–discharge curves (b) and cycle-life (filled square) and capacity retention (open square) at the current density of 1 A g^{-1} in 1 M KOH solution (c)

found that the Co₃O₄ nanoplates can deliver energy and power density of 0.038 and 0.715 W/g , respectively. These results confirm the high supercapacitive performance of Co₃O₄ nanoplates which is related to their porous morphology and high surface area.

4 Conclusions

In summary, Co_3O_4 with plate-like morphology was prepared via cathodic electrodeposition-heat treatment method. The prepared nanoplates displayed specific capacitance of as high as 393.6 F g^{-1} resulting from high surface area and effective utilization of Co_3O_4 . These characteristics indicate that Co_3O_4 nanoplates can be promising electroactive materials for supercapacitors.

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